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Synthesis and crystal structure of 5-carbaphosphatranes containing a four-membered cycle

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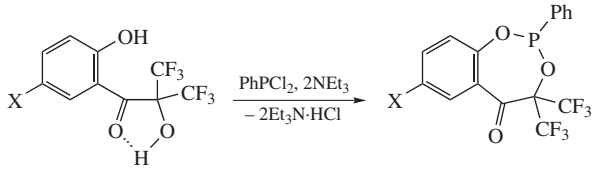
4,4-Bis(trifluoromethyl)-4,5-dihydro-2-phenylbenzo[*e*]- and 4,4-bis(trifluoromethyl)-4,5-dihydro-2-phenyl-(4′-chlorobenzo)[*e*]-1,3,2-dioxaphosphepin-5-ones react with hexafluoroacetone to form unusual propeller type structures – 3,3,10,10-tetrakis-(trifluoromethyl)-1-phenyl-6,7-benzo- and 3,3,10,10-tetrakis(trifluoromethyl)-1-phenyl-6,7-(4′-chlorobenzo)-2,4,8,9-tetraoxa-1-phosphatricyclo[3.3.2.0^{1,5}]decenes (5-carbaphosphatrane derivatives), the structure of which has been determined by NMR spectroscopy and single crystal X-ray diffraction analysis.

Phosphorus(III) derivatives containing a functional substituent, such as NCO, NCS, OC(O)R, C(R′)=CR$_2$ and C≡CR, are convenient precursors for various P-heterocyclic systems.[1–3] They include an activated multiple bond and easily react with unsaturated compounds, such as aldehydes, ketones, alkenes and imines *via* an initial nucleophilic attack of the phosphorus atom followed by a transfer of the reactive centre on the multiple bond of exocyclic substituent. At the same time, various rearrangements can take place.[1,2]

Here we have shown for the first time that P-heterocycles, bearing an endocyclic carbonyl group in the γ-position to phosphorus, can be used for the synthesis of the new heterocyclic system. We have synthesized new seven-membered heterocycles **3**, **4** (Scheme 1) by the phosphorylation of fluorinated hydroxyketones **1**, **2**, obtained according to published data,[4] with dichlorophenylphosphine in the presence of triethylamine. These unusual compounds contain two reactive centres: a nucleophilic phosphorus atom and an electrophilic carbonyl group. In spite of this fact, they are stable at 20 °C. NMR spectra confirmed their structure.

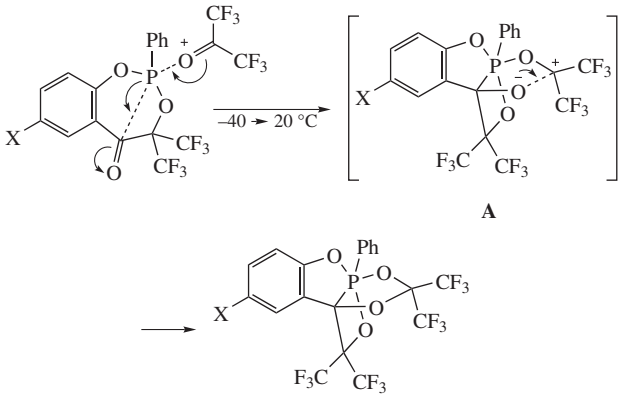


1 X = H
2 X = Cl

3 X = H
4 X = Cl

Scheme 1

The reaction of benzophosphepin-5-ones **3**, **4** with hexafluoroacetone leads to the formation of propeller-like pentacoordinated phosphorus species **5**, **6** bearing two five-membered and one four-membered rings, which are annelated along the common phosphorus–carbon bond (Scheme 2). Derivatives **5**, **6** are a new class of 5-carbaphosphatranes. Compounds containing only five- and six-membered cycles are known among them.[5–9] The reaction is likely to include an intramolecular attack of phosphorus on the endocyclic carbonyl group and a simultaneous interaction of the hexafluoroacetone carbonyl oxygen with phosphorus leading to the formation of intermediate **A**. Further attack of oxygen on carbon gives reaction products **5**, **6**.



5 X = H
6 X = Cl

Scheme 2

The structure of compounds **5**, **6** was established by a variety of correlation NMR methods (2D COSY-gp, 2D HSQC-gp, 2D HMBC-gp).† Analysis of these compounds was carried out in the identical way therefore only for **5** detailed description will be given.

The ^{1}H NMR spectrum of **5** consists of several signals of aromatic protons. Two groups of protons of benzo moiety and phenyl group uniquely stand out in the spectrum 2D COSY. The ^{13}C NMR chemical shifts of all hydrogenated carbons could be assigned unambiguously by the 2D HSQC spectrum.

The structures of the fragments of **5** were conclusively established based on HMBC correlations (Figure 1). The most important ones are between the protons at δ 7.53 (H^{11}), 7.16 (H^{14}) and the carbon resonance at δ 91.16 (C^5); the protons at δ 7.53 (H^{11}) and 7.45 (H^{13}) and the carbon resonance at δ 154.28 (C^7); the protons at δ 7.53 (H^{17}/H^{19}), and the carbon resonance at δ 133.86 (C^{15}).

Unfortunately, the rest of the carbons (C^{3,10}, C$^{21\text{-}24}$) cannot be assigned directly (non empirically) by 2D correlation techniques because these atoms are far away from the hydrogens and therefore there are no notable long-range spin-spin couplings to produce cross-peaks on these spectra. If to take into account that there are two electronegative oxygen atoms near to the C^3 and